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(54) Low-expanding cordierite quality ceramic composition

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(72) Inventor: Toshitaka Matsuura

c/o NGK Spark Plug Co., Ltd., No. 14 Lot. 18, Takatsujicho, Mizuho-ku, Nagoya-shi

(71) Applicant for Patent:

NGK Spark Plug Co., Ltd.,

No. 14 Lot. 18, Takatsujicho, Mizuho-ku, Nagoya-shi

(57) Scope of Claim for Patent:

1. A low-expanding cordierite quality ceramic composition formed by adding 0.1 - 10 parts of one oxide or more oxides selected from among Ta_2O_5, V_2O_5, Nb_2O_3, Cr_2O_3, MoO_3, and WO_3 to 100 parts of a base component composed of 10 - 20 weight % of MgO, 25 - 40 weight % of Al_2O_3, and 45 - 65 weight % of SiO_2.

Detailed Description of the Invention

This invention relates to a low-expanding cordierite quality ceramic composition.

The cordierite quality ceramics obtained by formulating refined starting raw materials, MgO, Al_2O_3, and SiO_3, into a composition of $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, forming the resultant mixed powder in a prescribed shape, and firing the formed mass of powder or by heating to melt the mixed powder once, pulverizing the resultant melt, and thereafter forming the produced powder in a prescribed shape, and firing the formed mass of powder possesses a markedly small thermal expansion coefficient as compared with other high purity oxide ceramics. Thus, this ceramics is finding extensive adoption as honeycombs proper for heat exchangers and as heat-resisting materials and thermal shock resisting materials such as for kettles and stoves.

This invention is based on the knowledge that the thermal expansion coefficient of the aforementioned cordierite composition formed of MgO, Al_2O_3, and SiO_3 can be further lowered to a level of not more than $20 \times 10^{-5}/°C$ by causisng the composition to contain therein a specific metal compound.

To be specific, the cordierite quality ceramics of this invention consists of a base component composed of 10 - 20 weight % of MgO, 25 - 40 weight % of Al_2O_3, and 45 - 65 weight % of SiO_2.and and at least one oxide selected from among Ta_2O_5, V_2O_5, Nb_2O_3, Cr_2O_3, MoO_3, and WO_3 and added in an amount in the range of 0.1 - 10 parts to 100 parts of the base component mentioned above.

Now, this invention will be described below with reference to working examples thereof.

Example 1

Refined MgO, Al_2O_3, and SiO_3 were weighed out in amounts

calculated to form a proportion shown in Table 1. A mixed powder obtained by adding 1.5 parts of Ta_2O_5 to the weighed oxides was heated and melted once at a temperature in the range of 1550 - 1650°C for one hour and suddenly cooled and vitrified. Subsequently, the produced glass was pulverized to not more than 250 mesh, and then press formed in a stated shape (5 mm × 9 mm × 30 mm) under a pressure of 500 kg/cm^2. Thereafter, the resultant shaped mass was heated in an oxidizing atmosphere at a temperature increasing rate of 5°C per minute to a level in the range of 950 - 1350°C, retained at this temperature for two hours till crystallization proceeded thoroughly, and gradually cooled to obtain a cordierite quality ceramic. This ceramic was tested for thermal expansion coefficient (25 - 800°C) and for water absorption. The results are shown in Table 1.

Table 1

Sample No.	Base component (weight %)			Additive (part by weight)	Thermal expansion coefficient	Water absorption (%)
	MgO	Al_2O_3	SiO_2	Ta_2O_3	($\times 10^{-6}/°C$)	
1	15	25	60	1.5	1.98	8.8
2	20	25	55	1.5	1.03	9.8
3	20	35	45	1.5	1.98	9.6
4	15	40	45	1.5	1.23	9.4
5	10	40	50	1.5	1.99	9.3
6	10	35	55	1.5	1.98	9.8
7	20	30	50	1.5	1.05	9.2
8	13	30	57	1.5	1.64	8.8
9	18	30	52	1.5	1.02	9.8
10	13.8	34.9	51.3	1.5	0.09	4.6
11	17.5	35	47.5	1.5	1.20	9.1
*12	10	27	66	1.5	2.3	8.0
*13	22	28	50	1.5	2.43	9.6
*14	15	43	42	1.5	2.48	9.1
*15	8	39	53	1.5	2.35	8.9
16	a commercially available cordierite quality ceramics				2.42	9.8

The asterisk (*) indicates an experiment deviating from the scope of this invention.

As shown in Table 1, the cordierite quality ceramics of this invention (Samples No. 1 - 11) composed of 10 - 20 weight % of MgO, 25- 40 weight % of Al_2O_3, and 45 - 60 weight % of SiO_2 and made to add thereto 1.5 parts by weight of Ta_2O_3 showed no appreciable effect in water absorption but a conspicuous improving effect in thermal expansion coefficient as compared with the ceramics having compositions outside the proper range of this invention (Samples No. 12 - 15) and a commercially available cordierite quality ceramics (Sample No. 16) and the sample of No. 10 showed these properties in

the smallest magnitudes.

Example 2

The cordierite quality ceramics manufactured by following the procedure of Example 1 while fixing the proportions of base components of the main component at those of the composition of Sample No. 10, i.e.13.8 weight % of MgO, 34.9 weight % of Al_2O_3, and 51.3 weight % of SiO_2, which manifested the most conspicuous effects and changing the amount of Ta_2O_3 in the experiment of Example 1 were tested for the properties mentioned above. The results were as shown in Table 2.

Table 2

Sample No.	Additive (part by weight)	Thermal expansion coefficient	Water absorption (%)	Remark
	Ta_2O_5	($\times 10^{-6}$/°C)		
*17	0	2.54	12.3	
*18	0.05	2.21	11.0	
19	0.1	1.90	9.3	
20	0.5	1.01	4.3	
21	1.5	0.90	4.6	Sample No. 10 of Table 1
22	2.0	0.91	5.1	
23	5.0	1.08	5.2	
24	7.0	1.38	6.1	
25	8.5	1.52	4.5	
26	10.0	1.99	4.0	
*27	12.0	2.30	5.4	

The asterisk (*) indicates an experiment deviating from the scope of this invention.

As shown in Table 2, the cordierite quality ceramics of this invention (Samples No. 19 - 26) made to contain 0.1 - 10 parts of Ta_2O_5 based on a total of 100 parts of MgO, Al_2O_3, and SiO_2 showed an improving effect in thermal expansion coefficient as compared with a ceramic omitting this addition

(Sample 17) and ceramics making this addition outside the range (Samples No. 17, 18, and 27) and particularly the cordierite quality ceramics of Sample No. 21 (Sample 10 of Table 1) which was made to add 1.5 parts of Ta_2O_5 showed the properties in the smallest magnitudes.

Example 3

Cordierite quality ceramics manufactured by following the procedure of Examples 1 and 2 while incorporating 1.5 parts of one or more oxides selected from among Ta_2O_5, V_2O_5, Nb_2O_5, MoO_3, and WO_3 in a base component composed of 13.6 weight % of MgO, 34.8 weight % of Al_2O_3, and 51.3 weight % of SiO_2 were tested for the properties mentioned above. The results were as shown in Table 3.

Table 3

Sample No.	Base component (part by weight)	Additive (part by weight)						Thermal expansion coefficient ($\times 10^{-6}/°C$)	Water absorption (%)
		V_2O_5	Nb_2O_5	Cr_2O_3	MoO_3	WO_3	Ta_2O_5		
28	100	1.5						1.01	6.3
29	100		1.5					1.08	7.5
30	100			1.5				1.18	6.5
31	100				1.5			1.30	7.2
32	100					1.5		1.16	6.8
33	100	0.75		0.75				1.10	7.1
34	100	0.75					0.75	1.01	7.1
35	100		0.75			0.75		1.12	6.9
36	100			0.75	0.75			1.10	6.7
37	100					0.75	0.75	0.98	6.4
38	100			0.5	0.5		0.5	1.40	6.5

As shown in Table 3, the cordierite quality ceramics having V_2O_5, Nb_2O_5, Cr_2O_3, MoO_3, and WO_3 singly contained therein as an oxide for addition to the base component composed of MgO, Al_2O_3, and SiO_2 (Samples No. 28 - 32) exhibited thermal

expansion coefficients approximating closely to that of the ceramics additionally incorporating Ta_2O_5 (Sample No. 10 in Table 2) and the ceramics having these oxides added in the form of a combination of two or more members as in Samples No. 33 - 38 exhibited equal effects.

The reason for this invention to limit the proportions of the base components, MgO, Al_2O_3, and SiO_2, respectively to the ranges of 20 - 20 weight %, 25 - 40 weight %, and 45 - 60 weight % is that the compositions falling in these ranges produce sinters which are formed mostly of cordierite crystals having small thermal expansion coefficients and manifest such effects as indicated in the brackets for Samples No. 1 - 11 in Table 1 and that the compositions falling outside the ranges produce sinters containing cordierite crystals in a small proportion and forsterite and other crystals in a larger proportion and, therefore, showing large thermal expansion coefficients as indicated in the brackets for Samples No. 12 - 15 in Table 1.

The reason for selecting Ta_2O_5, V_2O_5, Nb_2O_5, Cr_2O_3, MoO_3, and WO_3 as oxides for addition to the base component mentioned above is that one or more of these oxides manifest the effect of further improving the low expansion property of cordierite. This effect manifests conspicuously when the range of addition, 0.1 - 10 parts, based on 100 parts of the base component mentioned above is satisfied as indicated in the brackets for Samples No.19 - 26 in Table 2.

Since the cordierite quality ceramic compositions according to this inventions have such very small thermal expansion coefficients as falling below $20 \times 10^{-6}/°C$ as described above, they bring a great benefit when they are utilized for honeycomb structures in heat exchangers, for fire gratings in kettles and stoves, and for heat resisting

materials and shock resisting materials in heating units.

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発明の数　1

（全4頁）

1　2

⑤4低膨脹性コージライト質磁器組成物

㉑特　　願　昭49－111884

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⑦2発 明 者　松浦利孝

名古屋市瑞穂区高辻町14番18号日本特殊陶業株式会社内

⑦1出 願 人　日本特殊陶業株式会社

名古屋市瑞穂区高辻町14番18号

⑤7特許請求の範囲

1　重量%にてMgO 10～20%、Al_2O_3 25～40%、SiO_2 45～60%よりなる基盤成分100部に対しTa_2O_5、V_2O_5、Nb_2O_3、Cr_2O_3、MoO_3、WO_3のうちから1種又は2種以上を選んで0.1～10部添加してなる低膨脹性コージライト質磁器組成物。

発明の詳細な説明

本発明は低膨脹性コージライト質磁器組成物に関するものである。

出発原料として精製されたMgO、Al_2O_3、SiO_3を$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$組成に配合した混合粉末を所定形状に成形後焼成するか、あるいは焼成温度範囲を広くするために前記混合粉末を一旦加熱溶融して粉砕し、しかる後所定形状に成形して焼成して得たコージライト質磁器は、他の高純度酸化物磁器に比して熱膨脹係数が著しく小さいため熱交換器のハニカム機体を初めとしてカマ、ストーブ等の耐熱材料、耐熱衝撃材料として広く採用されている。

本発明は上記MgO、Al_2O_3、SiO_2よりなるコージライト組成に対し、特定の金属酸化物を添加含有させることによつて熱膨脹係数を一層小さく、2.0×10^{-6}／℃以下に引下げ得ることとの知見に基づくものである。

即ち、本発明コージライト質磁器は重量%にてMgO 10～20%、Al_2O_3 25～40%、SiO_2 45～60%よりなる基盤成分と、該基盤成分100部に対し0.1～10部添加含有せしめたTa_2O_5、V_2O_5、Nb_2O_3、Cr_2O_3、MoO_3、WO_3の1種以上とからなる。

以下本発明を実施例に基づいて説明する。

実施例　1

精製されたMgO、Al_2O_3、SiO_2を第1表に示す割合になるよう秤取し、これにTa_2O_5を1.5部添加せしめた混合粉末を一旦1550～1650℃で1時間加熱溶解すると共に急冷してガラス化し、続いてこのガラスを250メツシユ以下に粉砕した後所定形状（5㎜×9㎜×30㎜）に500kg／㎠の圧力でプレス成形し、しかる後この成形体を酸化雰囲気中にて毎分5℃の速度で950～1350℃まで昇温し、かつ結晶化が充分行なわれるまで2時間保持した後、除冷して得たコージライト質磁器について熱膨脹係数（25～800℃）と、吸水率を測定した結果を第1表に示す。

第　1　表

試料No.	基盤成分（重量%）			添加物（重量部）	熱膨脹係数（$\times 10^{-6}$／℃）	吸水率(%)
	MgO	Al_2O_3	SiO_2	Ta_2O_3		
1	15	25	60	1.5	1.98	8.8
2	20	25	55	〃	1.03	9.8

試料No.	基盤成分（重量%）			添加物（重量部）	熱膨脹係数（×10^{-6}／℃）	吸水率(%)
	MgO	Al_2O_3	SiO_2	Ta_2O_3		
3	20	35	45	1.5	1.98	9.6
4	15	40	45	〃	1.23	9.4
5	10	40	50	〃	1.99	9.3
6	10	35	55	〃	1.98	9.8
7	20	30	50	〃	1.05	9.2
8	13	30	57	〃	1.64	8.8
9	18	30	52	〃	1.02	9.8
10	13.8	34.9	51.3	〃	0.90	4.6
11	17.5	35	47.5	〃	1.20	9.1
※12	10	27	66	〃	2.3	8.0
※13	22	28	50	〃	2.43	9.6
※14	15	43	42	〃	2.48	9.1
※15	8	39	53	〃	2.35	8.9
16	市販品のコージライト質磁器				2.42	9.8

※印は本発明の範囲外

第1表に示される通り重量%にてMgO 10～20%、Al_2O_3 25～40%、SiO_3 45～60%からなり、これにTa_2O_3を1.5%重量部添加含有せしめた本発明のコージライト質磁器（試料No.1～11）は、本発明の適量範囲外の磁器（試料No.12～15）や市販のコージライト質磁器（試料No.16）に比して吸水率は然程効果はないが、熱膨脹係数については著しい改善効果を呈し、特にNo.10の試料は最小値を示した。

実施例 2

実施例1の結果に従い基盤成分の割合を最も著効が表われた試料No.10の組成、MgO 13.8重量%、Al_2O_3 34.9重量%、SiO_2 51.3重量%に主成分を固定し、これに加えるTa_2O_5の添加量を変化した以外は上記実施例1と同一条件で製作したコージライト質磁器について諸特性を測定した結果を第2表に示す。

第　2　表

試料No.	添加物（重量部）	熱膨脹係数（×10^{-6}／℃）	吸水率(%)	備考
	Ta_2O_5			
※17	0	2.54	12.3	
※18	0.05	2.21	11.0	
19	0.1	1.90	9.3	
20	0.5	1.01	4.3	
21	1.5	0.90	4.6	第1表の試料No.10

試料No.	添加物（重量部）	熱膨脹係数（×10^{-6}/℃）	吸水率(%)	備　考
	Ta_2O_5			
22	2.0	0.91	5.1	
23	5.0	1.08	5.2	
24	7.0	1.38	6.1	
25	8.5	1.52	4.5	
26	10.0	1.99	4.0	
※27	12.0	2.30	5.4	

※印は本発明の範囲外

上記第2表に示された通りMgO、Al_2O_3、SiO_2の基盤成分100部に対しTa_2O_5を0.1〜10部添加含有せしめた本発明のコージライト質磁器（試料No.19〜26）は、無添加の磁器（試料No.17）及び添加範囲外の磁器（試料No.17，18と27）に比して熱膨脹係数の改善に効果を示し、特に試料No.21（第1表の試料No.10）のようTa_2O_5を1.5部添加させたコージライト質磁器は最小値を示した。*

*実施例　3

実施例1、2の結果に従い、MgO 13.8重量%、Al_2O_3 34.8重量%、SiO_2 51.3重量%からなる基盤成分に対し、Ta_2O_5、V_2O_5、Nb_2O_5、M_0O_3、WO_3をそれぞれ一種または2種以上を1.5部配合せしめた以外は上記実施例1と同一条件で製作したコージライト質磁器の諸特性を測定した結果を第3表に示す。

第　3　表

試料No.	基盤成分（重量部）	添加物（重量部）						熱膨脹係数（×10^{-6}/℃）	吸水率(%)
		V_2O_5	Nb_2O_5	Cr_2O_3	M_0O_3	WO_3	Ta_2O_5		
28	100	1.5						1.01	6.3
29	〃		1.5					1.08	7.5
30	〃			1.5				1.18	6.5
31	〃				1.5			1.30	7.2
32	〃					1.5		1.16	6.8
33	〃	0.75		0.75				1.10	7.1
34	〃	0.75					0.75	1.01	7.1
35	〃		0.75			0.75		1.12	6.9
36	〃			0.75	0.75			1.10	6.7
37	〃					0.75	0.75	0.98	6.4
38	〃			0.5	0.5		0.5	1.40	6.5

第3表に示される通り、MgO、Al_2O_3、SiO_2基盤成分に添加する酸化物としてV_2O_5、Nb_2O_5、Cr_2O_3、M_0O_3、WO_3を各々単味で添加含有せしめたコージライト質磁器（試料No.

２８～３２）は、Ta_2O_5を添加した磁器（第２表中の試料№２１）と近似の熱膨脹係数を呈し、またこれら酸化物を複合の形で添加しても試料№３３～３８で示されるように同等の効果を示した。

而して本発明において基盤成分の割合を重量％にてMgO１０～２０％、$Al_2O_3$２５～４０％、$SiO_2$４５～６０％に限定した理由は、この範囲内の組成は焼結体の結晶の大部分が熱膨脹係数の小さいコージライト結晶であり第１表中試料№１～１１で示される通りの効果が得られ、また上記所定範囲外の組成はコージライト結晶が少なく、フオルステライト等他の結晶が多くなつて第１表中試料№１２～１５で示されるように熱膨脹係数が大きくなるからである。

また上記基盤成分に添加する酸化物としてTa_2O_5、V_2O_5、Nb_2O_5、Cr_2O_3、M_0O_3、WO_3、Ta_2O_5を選んだ理由は、これら酸化物の１種又は２種以上がコージライトの低膨脹性を更に一層改善する効果を発揮するからであるが、この効果は第２表中試料№１９～２６で示されるように上記基盤成分１００部に対し0.1～１０部の添加範囲内で顕著に表われた。

以上の通り本発明のコージライト質磁器組成物は熱膨脹係数が非常に小さく、20×10^{-6}／℃以下であるため熱交換器のハニカム構体、カマ、ストーブ等の火格子、その他発熱体等耐熱材料、耐衝撃材料に使用して大きな利益をもたらす。